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## Preface

# An overview of air-snow exchange at Summit, Greenland: Recent experiments and findings

## 1. Introduction

The research station at Summit, Greenland (72°34'N, 38°29'W, approximately 3250 masl) was established in 1989 for the recovery of the GISP2 ice core. At the time of its creation, the Summit station was 29 km east of, and 28 m lower than, the summit of the Greenland ice sheet (where the GRIP camp was established to recover the second of the summit ice cores). The steering committees of both ice core projects, and the international funding agencies, supported investigations of air–snow relationships in the region throughout the lifetimes of the GISP2 and GRIP project. Since the conclusion of GISP2 in 1993, the Summit camp has been maintained to support a range of scientific research, including ongoing air–snow investigations.

Physical and chemical characterization of the snow pack, and how these characteristics reflected variations in atmospheric composition and dynamics at Summit, has been a focus since the first campaign in summer, 1989. From the beginning, it was recognized that understanding air–snow relationships would be limited if sampling and observations were restricted to the summer seasons when it was easy to gain access to the Summit region (Dibb and Jaffrezo, 1997). In recognition of the value of winter-time observations, NSF OPP supported year-round investigations by small teams (two or three technicians conducting experiments for up to a dozen researchers) through the winter of 1997–98 and a 2-year campaign from August 2000 to August 2002. In August, 2003 the station was officially designated the Greenland Environmental Observatory at Summit (GEOSummit) and opened to support year-round measurements by the international scientific community. Funding is in place to

support operation through 2008, but it is hoped that the observatory will operate long into the future. The first section of this overview discusses selected results from year-round sampling at Summit, as presented more fully in seven papers in this special issue.

In the mid-1990s a series of intensive summer campaigns was initiated. These focused on improved understanding of how nitrogen oxide chemistry above Summit was reflected in the nitrate preserved in snow/firn and ice. It soon became apparent that the nitrogen oxide budget and cycling above the snow at Summit were perturbed compared to expectations for the remote free troposphere. In particular the  $\text{HNO}_3/\text{NO}_y$  ratio was found to be exceedingly small, leading to a hypothesis that organic nitrates might be the dominant source of nitrate in the snow (Dibb et al., 1998). A follow-up campaign to test this hypothesis led to the discovery that photolysis of nitrate in the snow produced  $\text{NO}_x$  which was released to the firn air and subsequently the boundary layer atmosphere above the snow (Honrath et al., 1999). Similar findings in the same year at Alert, NWT (Ridley et al., 2000), and South Pole (Davis et al., 2001) launched a series of investigations into snow photochemistry, including several intensive campaigns at Summit (Bottenheim et al., 2002). These campaigns have found that a host of reactive molecules are produced in sunlit snow and released into the atmosphere just above the snow, where they collectively create one of the most oxidizing regions of the troposphere through greatly enhanced production and abundance of  $\text{HO}_x$ . With the exception of the ISCAT campaigns at South Pole, where OH was measured (and confirmed to be very high (Mauldin et al., 2001, 2004)), the impact

of snow photochemistry and thermal desorption of precursors on  $\text{HO}_x$  (hence all atmospheric chemistry) above the snow was based on model calculations constrained by measured sources and sinks (e.g., Hutterli et al., 2001; Yang et al., 2002). Intensive sampling campaigns were conducted at Summit in summer 2003 and spring 2004 to directly test our understanding of  $\text{HO}_x$  cycling in this unusual environment. In addition to making the first measurements of OH,  $\text{HO}_2$ , and all presumed sources and sinks in the air just above the snow, these campaigns investigated photochemical processes within the surface snowpack. The second section of this overview presents highlights of these two campaigns, which are described more fully in five papers in this special issue.

## 2. Year-round measurements

### 2.1. Snow

During the 1997–1998 and 2000–2002 year-round campaigns significant effort was made to document the physical and chemical evolution of the snowpack at Summit. The technicians on site made observations of falling snow, clear sky precipitation (diamond dust), ice fog, and also any drifting or blowing of the surface layer every few hours. Surface height was measured weekly on 100 stakes on site and monthly on an additional 122 stakes along a 12 km transect to the southwest. Samples of the dominant layer of the surface snow were collected daily (weather permitting) for chemical and density measurements (conducted at several laboratories back in the US). At monthly intervals the top meter of the snowpack was sampled for the same chemical suite and detailed microphysical characterization, including determination of permeability on site.

Dibb and Fahnstock (2004) analyzed the stake measurements made in the 2000–2002 campaign and found that the relationship between surface height change and the accumulation of snow was complicated by seasonal changes in the rate of densification of the top meter of the snowpack. Enhanced densification during summer caused the rate of surface height increase to be smaller in this season, despite average, or above average, rates of snow accumulation. Dibb et al. (this issue) present the soluble ionic content of the daily surface snow samples collected in the 1997–1998 and 2000–2002 experiments. Their analysis focuses on seasonal

changes in snow composition, and confirms that the seasonality previously inferred from snowpit studies is largely valid. Specifically, the surface snow sampling found sharp April peaks in the delivery of dust to Summit, summer (June–August) peaks in  $\text{NH}_4^+$  and excess  $\text{Cl}^-$ , and a late winter (February–March) timing for the maximum delivery of seasalt. Comparisons between well-dated snowpits and simulated pits constructed from the surface samples suggest that the snowpack preserves on the order of 80% or more of the burden of most soluble ions delivered in snow at the surface, at least over periods up to 2 years. These comparisons suggest some loss of  $\text{NO}_3^-$ , but not more than 25% of the total delivered to the surface.

### 2.2. Atmosphere

Since 1997 air samples have been collected weekly at Summit, whenever it was occupied, as part of the NOAA/Earth Systems Research Laboratory/Global Monitoring Division's (ESRL/GMD formerly CMDL) Cooperative Global Air Sampling Network. Each sample consists of two glass flasks flushed in series with ambient air and then pressurized to  $\sim 1.3$  atm using a portable battery powered pumping apparatus. The samples are returned to the ESRL/GMD laboratory in Boulder, Colorado where each sample is analyzed for the mixing ratios of  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{CO}$ ,  $\text{H}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{SF}_6$ , and  $^{13}\text{C}/^{12}\text{C}$  and  $^{18}\text{O}/^{16}\text{O}$  in  $\text{CO}_2$ . The network and the analytical methods have been described in detail elsewhere (Conway et al., 1994; Dlugokencky et al., 1994; Novelli et al., 1992; Trolier et al., 1996).

The measurement time series for six species are shown in Fig. 1. The lack of high-frequency variability in the time series presented in Fig. 1 demonstrates that the atmosphere at Summit is, as expected, composed of well-mixed air masses not recently affected by local sources or sinks of the species measured. Through careful use of the portable air sampler the numerous people collecting samples over the years have been able to avoid sampling air contaminated by human activities at Summit camp. The time series in Fig. 1 contain signals due to processes occurring on large spatial scales in mid-to-high northern latitudes.

For example, the trends in  $\text{CO}_2$  (increasing) and  $\delta^{13}\text{C}$  (decreasing) are due primarily to  $\text{CO}_2$  emissions from combustion of fossil fuels (fossil carbon is depleted in  $^{13}\text{C}$  relative to the modern atmosphere). The near-mirror image seasonality of  $\text{CO}_2$

and  $\delta^{13}\text{C}$  is due to the seasonal imbalance between photosynthesis and respiration of the northern hemisphere terrestrial biosphere. In spring and summer, when photosynthetic uptake exceeds respiration,  $\text{CO}_2$  is removed from the atmosphere. Plants using the C3 photosynthetic pathway discriminate against  $^{13}\text{CO}_2$ , so the atmosphere becomes relatively enriched in  $^{13}\text{C}$ . When respiration exceeds photosynthesis  $\text{CO}_2$  enriched in  $^{12}\text{C}$  is returned to the atmosphere. The scaling factor used in panels 1a and 1b,  $0.05\% \text{ ppm}^{-1} \text{ CO}_2$ , is characteristic of C3 plants. Simultaneous measurements of atmospheric  $\text{CO}_2$  mixing ratio and  $\delta^{13}\text{C}$  of  $\text{CO}_2$  provide a strong constraint for quantitative estimates of the marine and terrestrial sinks for fossil fuel  $\text{CO}_2$  (Ciais et al., 1995).

After increasing by more than a factor of 2 since pre-industrial times, the rate of increase of  $\text{CH}_4$  (Fig. 1c) has been essentially zero since 1999. Dlugokencky et al. (2003) suggested that a balancing of  $\text{CH}_4$  sources and sinks has resulted in a new steady-state atmospheric burden.  $\text{CO}$ , which has the shortest lifetime of the gases measured in these air samples, also shows no significant trend in recent years (Novelli et al., 2003).  $\text{N}_2\text{O}$  and  $\text{SF}_6$ , both infrared absorbing (“greenhouse”) gases, are increasing steadily at  $0.7 \pm 0.1$  and  $0.21 \pm 0.01$  ppt year $^{-1}$ , respectively. The primary cause of  $\text{N}_2\text{O}$  increase is agricultural use of nitrogen fertilizers.  $\text{SF}_6$  is primarily used as an insulator in electrical switches and atmospheric  $\text{SF}_6$  measurements are often used as a tracer for anthropogenic influence on air masses as well as a constraint on atmospheric transport models.

Similarly, the Blake group at UC Irvine has been providing stainless steel canisters for whole air sampling at Summit whenever possible. A metal bellows pump was installed in the science trench and samples were drawn down a stainless steel line into the canisters, pressurized to about 20 psi. The samples were returned to the UC Irvine lab for analysis for an extensive suite of gases by GC FID/ECD/MS (see Colman et al. (2001) for details of the analysis).

All the gases in Figs. 2–4 show substantial seasonal variation. Consistent with previous work (e.g., Penkett et al., 1993; Swanson et al., 2003), the longer-lived gases tend to have lower amplitude seasonal swings. All the gases build up over the winter as the result mainly of the weaker OH sink but the longer-lived ones, e.g., ethane, reach their minimum values later in the summer (Fig. 2).

The time series for  $\text{C}_2\text{Cl}_4$ , ethyne, ethane and propane (Fig. 3) show that only  $\text{C}_2\text{Cl}_4$  displays an obvious long-term trend, declining by about 6 pptv over the 7 year observation period, or an average of about  $0.9 \text{ pptv year}^{-1}$ . This observation is consistent with the 30% decrease in annual global  $\text{C}_2\text{Cl}_4$  mixing ratios between 1995 and 2002 reported by Simpson et al. (2004).

The atmospheric alkyl nitrate seasonal variation at Summit has been described by Swanson et al. (2003) using a single year of measurements (1997–1998). By contrast, Fig. 4 includes a much more comprehensive set of data. The new multi-year plots reveal very similar seasonal variations to those reported by Swanson et al. (2003) but more convincingly define the seasonal cycles of all four alkyl nitrates, particularly that of methyl nitrate.

The seasonal variations of the non-methane hydrocarbons and alkyl nitrates should be sensitive to long-term changes in combustion (and other) sources, as well as the oxidizing capacity of the troposphere. The multi-year hydrocarbon and alkyl nitrate data provide crucial baseline information with which to detect long-term changes that may occur in sources or sinks in the future.

The time series presented in Figs. 1 and 3 clearly demonstrate the suitability of Summit for measurements of gases representative of large well-mixed air masses. The value of these records is currently limited because they are short and contain large gaps. Longer, continuous records from Summit, combined with data from the global network, will help better constrain estimates of trace gas budgets, and provide deeper understanding of the processes underlying the observed atmospheric variability. The observation that many of the sparingly soluble trace gases display smooth seasonal cycles that reproduce themselves almost exactly year to year (e.g. Figs. 2 and 4), also confirms that Summit is an excellent vantage point from which to obtain samples that are representative of the high-latitude northern hemisphere.

The aerosol-associated radionuclide tracers  $^7\text{Be}$  and  $^{210}\text{Pb}$  have also been quantified in all year-round campaigns at Summit (Dibb, this issue). Like the long-lived gases shown in Fig. 1, the activities of these tracers in the remote free troposphere should generally reflect large-scale mixing, in this case between air masses originating in the upper troposphere/lower stratosphere (UT/LS) ( $^7\text{Be}$ ) and those from the continental boundary layer ( $^{210}\text{Pb}$ ).

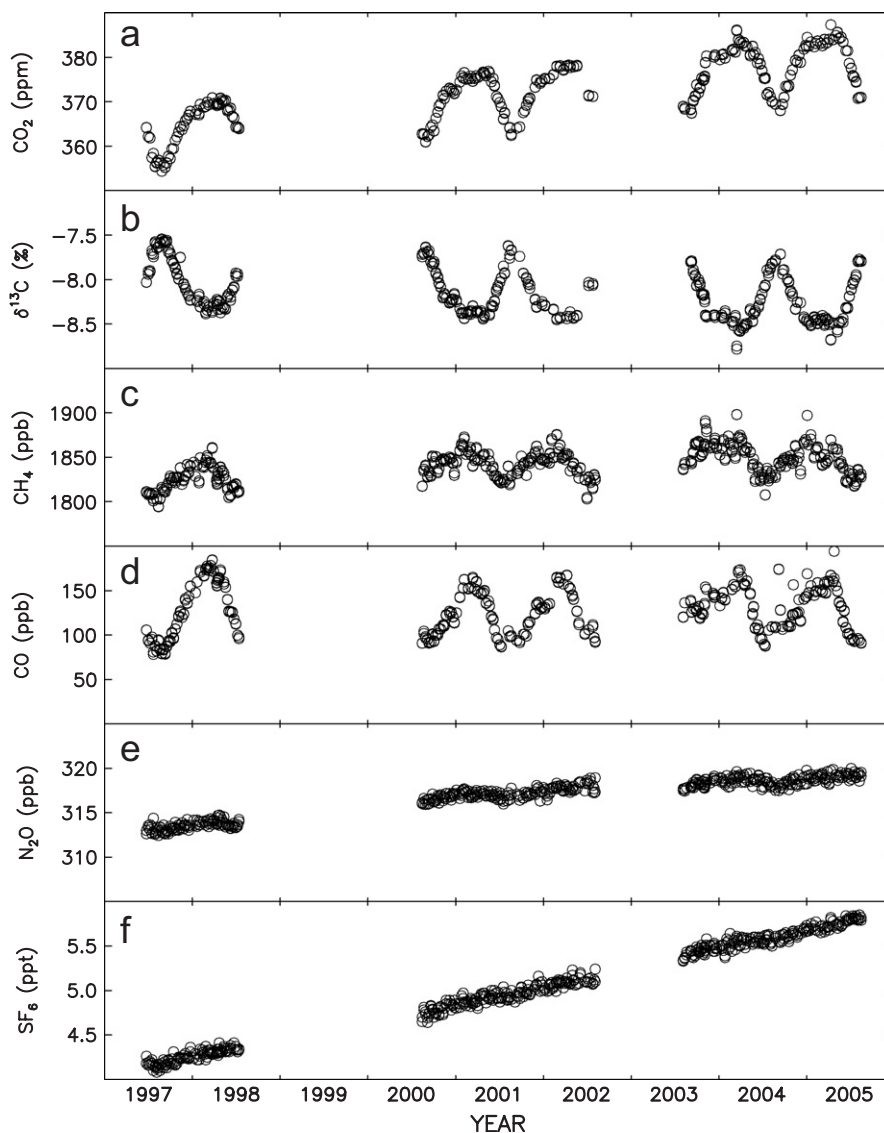


Fig. 1. Example time series from Summit sampling as part of the NOAA/Earth Systems Research Laboratory/Global Monitoring Division's (ESRL/GMD formerly CMDL) Cooperative Global Air Sampling Network. Each symbol represents the measurement of a single flask. The species plotted and their analytical repeatabilities ( $1\ \mu$ ) are: (a)  $\text{CO}_2$  (0.07 ppm), (b)  $\delta^{13}\text{C}$  (0.01 ‰), (c)  $\text{CH}_4$  (1 ppb), (d)  $\text{CO}$  (2 ppb) (e)  $\text{N}_2\text{O}$  (0.2 ppb) and (f)  $\text{SF}_6$  (0.04 ppt).

However, at Summit the time series of these tracers are dominated by high-frequency variability (Fig. 5). If this high-frequency “noise” is smoothed by taking monthly averages, a strong and reproducible summer peak in  $^7\text{Be}$  becomes obvious, and is suggested to reflect a significant UT/LS contribution to the air reaching Summit during this season (Dibb, *this issue*). Helmig et al. (*this issue a*) show that seasonal variations in  $\text{O}_3$  mixing ratios, and the relationships between  $\text{O}_3$ ,  $^7\text{Be}$  and water vapor are also consistent with downwelling UT/LS air masses

exerting strong influence on the summertime composition of air at Summit.

It should be noted that the high-frequency variability in the radionuclide tracers provides important insight into boundary layer dynamics at Summit. Activities of these tracers have been shown to decrease over time under very stable conditions (on the Greenland ice sheet), and to increase rapidly when the near-surface inversion breaks down and the boundary layer is replenished by air from aloft (Dibb, 1990, *this issue*; Dibb and Jaffrezo, 1993;

Dibb et al., 1992). Comparison to a single year of sampling at DYE 3 in south Greenland indicates that the surface air at Summit is, on average, better isolated from the free troposphere (Dibb, *this issue*), but the large sample to sample changes in the activities of  $^7\text{Be}$  and  $^{210}\text{Pb}$  at Summit (Fig. 5) indicate that strong capping inversions rarely persist for very long. Cohen et al. (*this issue*) combine micrometeorological measurements from short towers and from tether sondes deployed at Summit through several spring and summer seasons to show that strongly stable conditions rarely persist more than 24 h in spring, and become even less persistent in summer. Positive values of sensible heat flux around mid-day (7:00–18:00 local time) through the summer dominate the surface energy balance and often lead to a weakly unstable boundary layer (51% of observations in July and August). At night, the boundary layer height decreases dramatically as radiative cooling reestablishes strongly stable conditions. Cohen et al. (*this issue*) specifically contrast boundary layer dynamics at Summit and South Pole and suggest that the stronger, and more persistent, stability at South Pole explains much of the difference in boundary layer chemistry at the two sites.

The contrasting behavior of the trace gases shown in Figs. 1–4, which dominantly reflect long-range transport and chemical processing in the free troposphere, and the radionuclide tracers, with strong overprinting by boundary layer processes at Summit, is due to the fact that the aerosols carrying  $^7\text{Be}$  and  $^{210}\text{Pb}$  are lost by deposition to the underlying snow and become depleted under persistent inversions.

The snow surface plays an active role in atmospheric chemistry, serving as a strong sink for aerosols and also “sticky” gases (e.g.,  $\text{HNO}_3$  (Dibb et al., 1998; Honrath et al., 2002)). The snow at Summit has been shown to destroy  $\text{O}_3$  at a very rapid rate when the sun is high (Peterson and Honrath, 2001; Helmig et al., *this issue b*). On the other hand, there is mounting evidence that sunlit snow can act as a source of an ever growing number of reactive gases.

Swanson et al. (2007, *this issue*) present evidence for production of alkyl halides in the snow at Summit, South Pole, and two shallow seasonal snowpacks in the temperate zone of North America. Mixing ratios of alkyl halides in firn air at Summit were higher than at South Pole, apparently due to higher concentration of organic carbon in the snow.

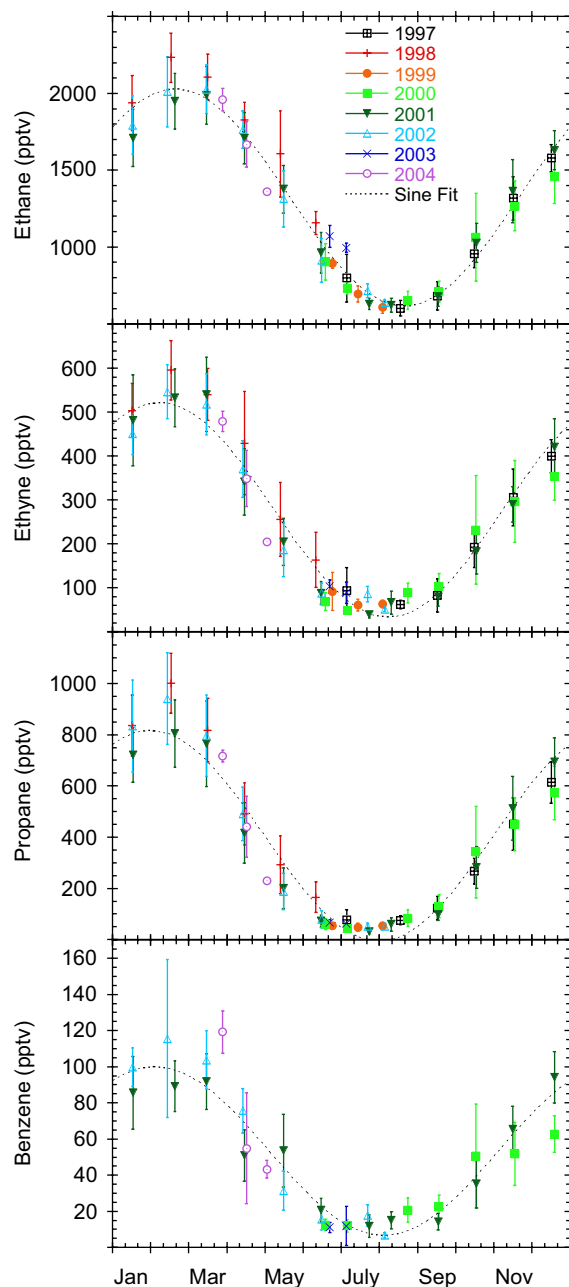


Fig. 2. Monthly average  $\pm$  1SD mixing ratios for ethane, ethyne, propane and benzene vs. day of year for all UCI samples collected at Summit between summer 1997 and summer 2004.

A postulated soil source appears to overwhelm production in the snow at the mid-latitude sites, leading to very high mixing ratios of some alkyl halides. The data set on alkyl halides in firn air at Summit is the most extensive, and shows a direct relationship between their abundance and solar irradiance, suggesting that a photochemical process



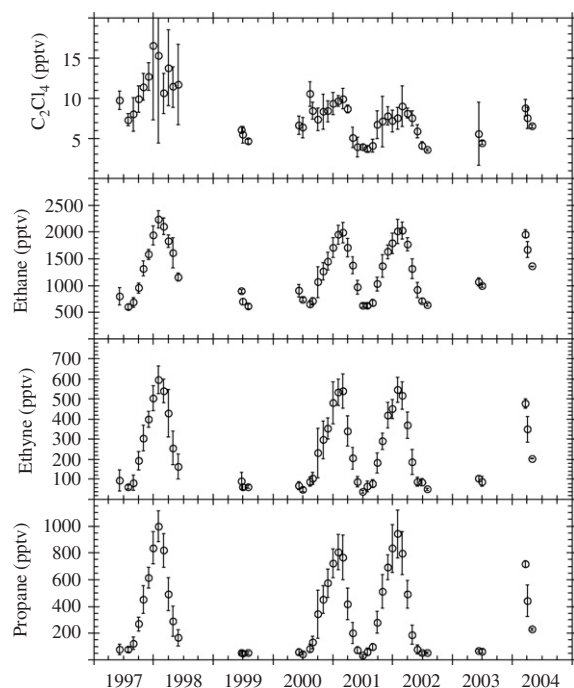


Fig. 3. Long-term trends in monthly average  $\pm$  1SD mixing ratios in UCI samples for  $C_2Cl_4$ , ethane, ethyne, and propane plotted vs. date for all samples collected at Summit between summer 1997 and summer 2004.

is producing them from halogen and organic precursors in the snow (Swanson et al., 2007, this issue).

Gases produced in the snow, released into firn air and then into the boundary layer have been the focus of a series of intensive sampling campaigns; in Antarctica, the Canadian Arctic, as well as Summit. The most recent Summit snow photochemistry campaigns are the focus of nearly half the papers in this special issue and we turn now to a summary of the key findings from these campaigns.

### 3. Summit snow photochemistry, summer 2003 and spring 2004

These intensive sampling campaigns targeted two related, but distinctive objectives. One priority was to test our understanding of  $HO_x$  cycling in the air above the snow at Summit, by making simultaneous measurements of  $OH$ ,  $HO_2 + RO_2$ , and the suite of reactive gases currently felt to constitute the important  $HO_x$  precursors and sinks. Several of the reactive gases are known to be elevated at Summit due to fluxes out of the snow (e.g.,  $NO_x$ ,  $HONO$ ,  $HCHO$ ,  $HOOH$ ). The second priority

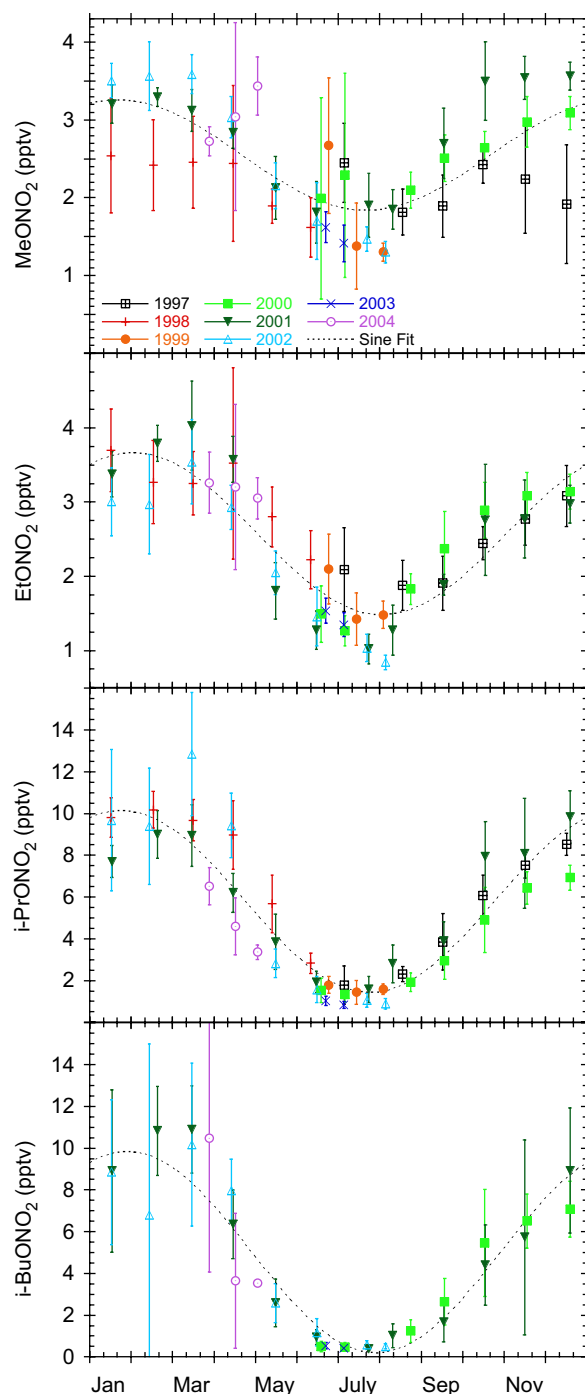


Fig. 4. Monthly average  $\pm$  1SD mixing ratios for methyl, ethyl, *i*-propyl and *i*-butyl nitrates vs. day of year for all UCI samples collected at Summit between summer 1997 and summer 2004.

objective was to improve our understanding of the chemistry occurring within the snowpack, both on snow grains and within the firn air filling pores between snow grains.

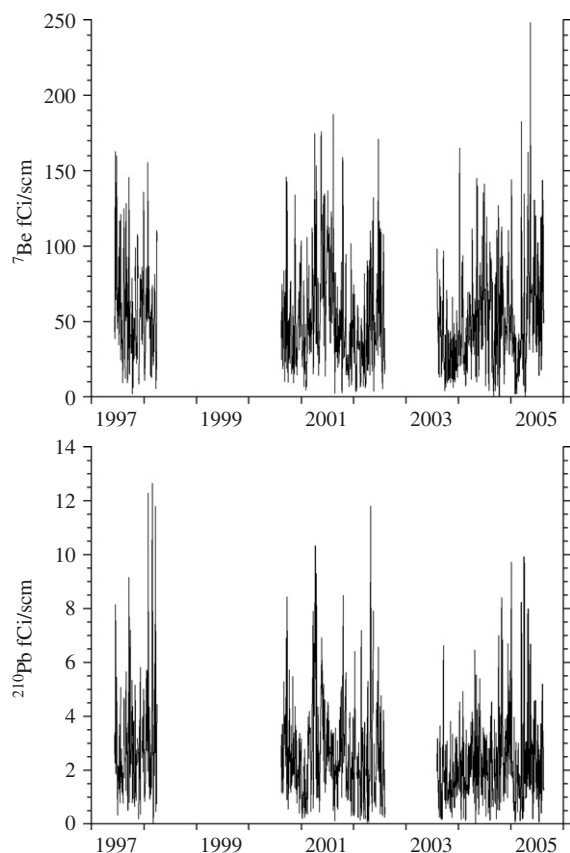


Fig. 5. Activities of the radionuclide tracers  $^7\text{Be}$  and  $^{210}\text{Pb}$  at Summit, from 2 day long filter exposures (see also Dibb, [this issue](#)).

Campaigns were conducted in mid-summer and in spring to encounter a wide range of actinic flux and also temperature. Previous work has shown that many of the reactive gases of interest display large diel cycles, both in the firn air and in the atmosphere just above the snow. Some have interpreted these variations as evidence that production in the snowpack is primarily photochemical (e.g., [Sumner and Shepson, 1999](#); [Domine and Shepson, 2002](#)), while others have argued that thermal sorption/desorption exerts primary control on the mixing ratios of gases that partition between ice and firn air (e.g., [Hutterli et al., 2003](#)). Unraveling these processes has been difficult, since temperature increases with greater solar flux (albeit with a time lag that increases with depth in the snowpack).

The contrast between mid-summer and spring is large ([Fig. 6](#)), and is particularly striking if the mixing ratios of  $\text{HO}_x$  precursors in shallow firn air are compared. However, it should be noted that

throughout the mid-day period in both seasons, the mixing ratios of  $\text{HCHO}$ ,  $\text{HOOH}$  and  $\text{HONO}$  are significantly higher 5 cm into the snowpack than they are at deeper depths. This enhancement in shallow firn is greater in summer, when both the actinic flux and the temperature are higher, but even in spring the shallow firn appears to be a strong source of reactive gases for the overlying atmosphere.

Close inspection of [Fig. 6](#) reveals subtle, but important, differences in the diel patterns of the three gases in shallow firn. The timing of the peak mixing ratios shifts later in the day for  $\text{HCHO}$  than  $\text{HONO}$ , with a hint of an even later peak in  $\text{HOOH}$ . Nitrous acid peaks near local solar noon, and decreases in phase with  $j\text{-NO}_2$  (though not as smoothly), while  $\text{HOOH}$  mixing ratios track the change in temperature more closely. The diel cycle of  $\text{HCHO}$  at 5 cm depth resembles the sum of the photon flux and temperature curves more closely than it does either individual curve, while at 25 cm depth the  $\text{HCHO}$  mixing ratio closely tracks temperature. These patterns suggest that photochemical production is the dominant source of  $\text{HONO}$  in firn air, while thermal desorption is more important for  $\text{HOOH}$ . Formaldehyde may be showing comparable effects from both processes at shallow depths, with increasing control by temperature deeper where the light is more attenuated. It should be noted that  $\text{NO}_x$ , particularly  $\text{NO}$ , tracks actinic flux even more closely than does  $\text{HONO}$ . Analysis of much additional data from firn air sampling in both seasons is ongoing and will be presented in forthcoming papers (e.g., [Hutterli et al., "Concentrations of reactive gases in firn air: relationships to temperature and actinic flux"](#), to be submitted to *Atmospheric Environment*).

A critical component to understanding photochemistry in the sunlit snowpack is improved knowledge of the actinic flux at different depths. We used two different techniques to measure sunlight profiles in the snowpack: a new chemical actinometry approach using acetonitrile/water as the solvent for mixtures of different OH-generating chromophores and benzene, and a spectroradiometer with multiple fiber optic irradiance probes to sample UV–vis radiation at multiple depths. [Galbavy et al. \(this issue a, b\)](#) present the details of the chemical actinometry and spectroradiometry methods of determining snowpack photolysis frequencies. Comparison of the two techniques to each other, and to photolysis frequencies calculated with



actinic flux derived from the TUV radiative transfer model, found reasonable agreement for the quantification of  $j\text{-NO}_3^-$  and  $j\text{-HOOH}$  in the snowpack. These comparisons also revealed unexpected complications in the use of the actinometry technique for determination of  $j\text{-NO}_2^-$ . Both of the measurement techniques confirmed large enhancements in photolysis frequencies right at the snow surface due to multiple reflections of downwelling photons. Similarly, both techniques found that the e-folding depths increased from about 12 cm for  $j\text{-NO}_3^-$  and  $j\text{-HOOH}$  to 16 cm for  $j\text{-NO}_2^-$ , consistent with the shift in action spectra to longer wavelengths where attenuation by snow decreases.

The very short lifetime of OH currently precludes measuring it within firn air. [Beyersdorf et al. \(this issue\)](#) report on an approach to constrain OH mixing ratios in firn air by monitoring the relative rates of destruction of a suite of introduced butenes, chosen to have a range of OH reactivities but similar diffusivities, while [Anastasio et al. \(this issue\)](#) used ice pellets doped with benzoate to constrain the rate of OH formation in/on ice surfaces in the near-surface snowpack. [Beyersdorf et al. \(this issue\)](#) found that their estimate of OH increased with solar flux, on both diel and seasonal cycles. The highest values were reached shortly after noon in early July ( $3.2 \times 10^6 \text{ mol cm}^{-3}$ ), with a minimum that same day near  $1 \times 10^6 \text{ mol cm}^{-3}$ . In contrast, the maximum on 15 April was  $1 \times 10^6$  and by 1 May the daily peak had increased to  $1.5 \times 10^6 \text{ mol cm}^{-3}$ . Mixing ratios of OH in firn air were comparable to those above the snow in spring, but by mid-summer the atmospheric levels were about twice those estimated in firn air.

[Anastasio et al. \(this issue\)](#) measured OH photoformation rates in their ice pellets on the snow surface around  $200 \text{ nmol L}^{-1} \text{ h}^{-2}$  in summer. These rates agreed closely with rates calculated from photolysis of  $\text{NO}_3^-$  and HOOH (using measured snow concentrations and  $j$ -values calculated by TUV). More than 95% of the production of OH was attributed to the photolysis of HOOH at the surface, and this source was even more dominant when integrated over the top 20 cm of the snowpack. The calculations also suggest that more than 90% of OH production on snow grains in the snow pack occurs in the top 10 cm, as  $j\text{-HOOH}$  decreases rapidly with depth.

Regarding our understanding of  $\text{HO}_x$  in the air above the snow, [Sjostedt et al. \(this issue\)](#) present the first measurements of OH and  $\text{HO}_2 + \text{RO}_2$  on

the Greenland ice sheet. As expected, the levels are quite high, with overall medians for the summer of 2003 of  $2.6 \times 10^8 \text{ mol (HO}_2 + \text{RO}_2) \text{ cm}^{-3}$  and  $6.9 \times 10^6 \text{ mol OH cm}^{-3}$ . Note that for OH these values are nearly four times higher than observed at South Pole ([Mauldin et al., 2001, 2004](#)). If attention is restricted to several hours surrounding local noon, the medians at Summit increase to  $4.1 \times 10^8$  and  $8.4 \times 10^6 \text{ mol cm}^{-3}$  of  $\text{HO}_2 + \text{RO}_2$  and OH, respectively.

[Sjostedt et al. \(this issue\)](#) compared the  $\text{HO}_x$  observations to a fully constrained photochemical box model (the model used all available measurements of NO, HONO, HOOH, HCHO,  $\text{O}_3$ ,  $j$ -values, temperature, etc. and calculated the  $\text{HO}_x$  species). The median value of the ratio (model estimated  $\text{HO}_2 + \text{RO}_2$ )/(the observed value) (M/O) was 1.16 and the values were strongly correlated ( $r^2 > 0.7$ ), suggesting that our understanding of  $\text{HO}_x$  source and sinks during the summer at Summit is reasonable. Interestingly, this analysis found photolysis of  $\text{O}_3$  to be the major  $\text{HO}_x$  source, unlike the earlier model study by [Yang et al. \(2002\)](#). The calculations reported by [Yang et al. \(2002\)](#) were constrained by observations from the 1999 and 2000 seasons at Summit (but lacked  $\text{HO}_x$  observations) and found that elevated mixing ratios of HOOH, HCHO and HONO (from the snow) enhanced  $\text{HO}_x$  production rates more than three fold compared to just  $\text{O}_3$  photolysis. In contrast, similar comparisons between observation and model predictions at South Pole found HCHO and HOOH emitted from the snow to account for nearly half of the  $\text{HO}_x$  source, with equal contributions from  $\text{O}_3$  and  $\text{CH}_4$  making up the balance ([Chen et al., 2004](#)).

Despite the success of the model at predicting  $\text{HO}_2 + \text{RO}_2$  at Summit, predicted OH was consistently 2–3 times lower than the observed values ([Sjostedt et al., this issue](#)). The discrepancy between modeled and observed OH increased dramatically during periods of high wind and blowing snow. During one such event observed OH exceeded  $2 \times 10^7 \text{ mol cm}^{-3}$  (accompanied by a 5 ppb drop in  $\text{O}_3$  and a decrease in  $\text{HO}_2 + \text{RO}_2$  to  $2 \times 10^8 \text{ mol cm}^{-3}$ ). Because we have several indirect lines of evidence suggesting that halogen chemistry may be important at Summit, [Sjostedt et al. \(this issue\)](#) added a bromine reaction scheme to the photochemical model and tested the impact of assuming the presence of modest amounts of BrO. Assuming an average abundance of 5 pptv of BrO improves the median M/O ratio for OH (in fully constrained

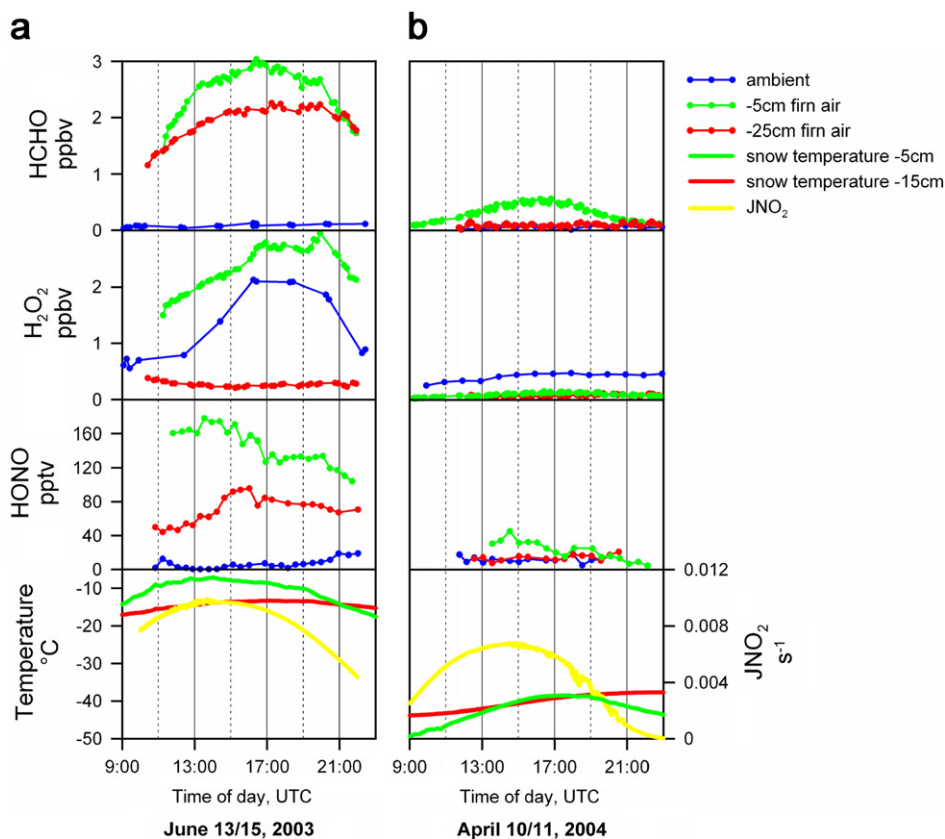


Fig. 6. Comparison of mixing ratios of selected  $\text{HO}_x$  precursors in ambient and firn air at Summit on two example days. Temperature and  $j\text{-NO}_2$  values are also shown. (a) is from mid-summer 2003 while (b) is from the spring 2004 campaign.

model runs on a filtered data set) from 0.58 to 0.68, while 10 pptv BrO yields median M/O of 0.83. Encouragingly, the addition of 10 pptv BrO also improves the median M/O for  $\text{HO}_2 + \text{RO}_2$  from 1.23 to 1.18.

#### 4. Conclusions

Summit, Greenland has an illustrious history in both ice core and air-snow exchange research. As the International Greenland Environmental Observatory at Summit, this site also appears to have a bright future. Year-round sampling programs like those discussed herein are ongoing, and NOAA is continually expanding their suite of year-round measurements. In late winter 2005, NOAA was able to observe the recovery of stratospheric  $\text{O}_3$  through profiles obtained from sondes launched at Summit, this year supplies and personnel are in place to launch  $\text{O}_3$  sondes from Summit through the Arctic winter. Future snow photochemistry cam-

paigns are already funded or have been proposed. For example, sampling and experimentation to quantify the impact of photochemical processing on organic compounds delivered to the surface planned for 2006 will follow up on observations of the decay of several specific organic chromophores conducted in 2005. These investigations represent the first steps toward understanding how snow photochemistry modifies the record of organic aerosols that may be recovered from ice cores. Similarly, atmospheric and snow sampling to constrain the processes controlling the isotopic composition of nitrate at Summit were begun in 2005 and will be expanded in the future. Several of the authors of this overview and companion papers in this issue have proposed a collaborative campaign to confirm or refute the postulated importance of halogen chemistry as a control on  $\text{HO}_x$  cycling at Summit (perhaps by extension demonstrating a key role for halogen chemistry throughout the free troposphere, or at least over most

snow-covered terrain). Please share our excitement about the results from this unique site, and consider joining us in future research efforts on top of the Greenland ice sheet.

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